

PATENT APPLICATION

METHOD AND APPARATUS FOR UV EXPOSURE OF LOW  
DIELECTRIC CONSTANT MATERIALS FOR POROGEN REMOVAL  
AND IMPROVED MECHANICAL PROPERTIES

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# METHODS OF POROGEN REMOVAL FOR POROUS LOW DIELECTRIC CONSTANT FILMS USING PLASMA TREATMENTS

## CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part claiming priority under 35 USC 120 from US  
Patent Application No. \_\_\_\_\_, (Attorney Docket No. NOVLP089), filed on March  
11, 2004, titled "Method and Apparatus for UV Exposure for Porogen Removal and Film  
Hardening for Application in Formation of Porous Ultra-Low Dielectric Constant  
10 Materials," by Easwar Srinivasan et al., which application is incorporated herein by  
reference in its entirety for all purposes. This application is also related to US Patent  
Application No. 10/672,311, filed on September 26, 2003, titled "Method of Porogen  
Removal from Porous Low-k Films using UV Radiation," by Adrienne Tipton et al.; US  
Patent Application No. 10/404,693, filed on March 31, 2003, titled "Method for Forming  
15 Porous Films by Porogen Removal Combined with In Situ Surface Modification," by  
Raashina Humayun et al.; and US Patent Application No. 10/672,305 filed on September 26,  
2003, titled "Method for Removal of Porogens from Porous Low-k Films Using  
Supercritical Fluids," by Adrienne Tipton et al., which applications are incorporated herein  
by reference in its entirety for all purposes.

## FIELD OF THE INVENTION

This invention relates to methods and apparatus for preparing porous low-k dielectric films for, e.g., integrated circuits. Additionally, the invention relates to methods of removing porogen from low-k dielectric precursor film.

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## BACKGROUND

There is a general need for materials with low dielectric constants (low-k) in the integrated circuit manufacturing industry. Using low-k materials as the inter-metal and/or inter-layer dielectric between conductive interconnects reduces the delay in signal  
10 propagation due to capacitive effects. The lower the dielectric constant of the dielectric material, the lower the capacitance of the dielectric and the lower the RC delay of the integrated circuit (IC).

Low k dielectrics are conventionally defined as those materials that have a dielectric constant lower than that of silicon dioxide, that is  $k < 4$ . Typical methods of obtaining low-k  
15 materials include doping silicon dioxide with various functional groups containing carbon or fluorine. While fluorinated silicate glass (FSG) generally has k of 3.5 – 3.9, carbon-doping methods can further lower the k value to ~2.6. However, with more stringent constraints imposed by advancing technology needs, present efforts are focused on developing dielectric materials with k values less than 2.5. These ultra low-k (ULK) dielectrics can be obtained  
20 by incorporating air voids within a low-k dielectric matrix to thereby create a porous dielectric material.

Methods of fabricating porous dielectrics typically involve forming a composite film (sometimes referred herein as a “precursor film”) containing two components: a porogen (typically an organic material such as a polymer or polyfunctional cyclic hydrocarbon) and a  
25 structure former or dielectric material (e.g., a silicon oxide containing material). Once the composite film is formed on the substrate, the porogen component is removed, leaving a structurally intact porous dielectric matrix. Techniques for removing porogens from the composite film include, for example, thermal processes in which the substrate is heated to a temperature sufficient for the breakdown and vaporization of the organic porogen.  
30 Unfortunately, thermal processes have certain difficulties. In particular, substrate temperatures generally need to be high (i.e., greater than about 400 degrees Celsius) with

exposure times typically on the order of hours. As is well known in the field, these conditions can damage copper containing electronic devices. To address these difficulties, US Patent Application No. 10/672,311, by Tipton et al. (which application was previously incorporated by reference) discloses methods for removing porogen material from a precursor film using UV radiation.

Once the porogen component is removed from the precursor film, the resulting dielectric film contains voids and reduces the overall dielectric constant of the film. However, this general approach will also reduce the density of the film and may sacrifice the mechanical strength and thermo-mechanical properties of the film. Since dielectric films can be subjected to severe thermal and mechanical conditions in IC processes such as chemical mechanical polishing (CMP) and packaging, these porous films need to have sufficient mechanical strength to withstand these processes. To address these issues, US Patent Application No. \_\_\_\_\_ (Attorney Docket No. NOVLP089), by Srinivasan et al. (which application was previously incorporated by reference) describes UV radiation exposure methods to increase the mechanical strength of low-k porous films. In that application, it is shown that UV radiation can strengthen the dielectric network of the low-k porous film, possibly by partially reconstructing bonds within the film.

Thus, UV radiation can provide at least two functions in producing porous dielectric materials: removing porogen from the precursor layer and mechanically strengthening the dielectric matrix. Two issues encountered when using UV radiation to treat precursor films are that the UV curing time can be long and the UV reaction chamber can become coated with porogen residues, including the windows that allow UV light to reach the wafer. After time these porogen residues can reduce the effectiveness of the subsequent UV treatments. Thus, UV treatment chambers may require frequent cleaning, thereby lowering wafer throughput.

What are therefore needed are ways to ensure that processing chambers (*e.g.*, UV chambers and e-beam chambers) used for treating porous low-k materials to increase the mechanical strength of the materials remain clean during the manufacturing process and that throughput remains high.

## SUMMARY

The present invention addresses this need by providing improved methods for preparing a low-k dielectric film on a substrate using a separate plasma treatment or an in-situ plasma treatment to remove at least some porogen before a treatment to further remove porogen and/or improve the strength of the films using, for example, UV radiation. In particular, some methods involve (a) forming a precursor film on the substrate in a first chamber, (b) exposing the precursor film to a plasma in the first chamber to remove at least a substantial portion of the porogen from the precursor film and (c) treating the substrate in a second chamber to increase the mechanical strength of the porous low-k dielectric film. Note that the precursor film includes a porogen and a structure former. In some embodiments, operation (c) also serves to remove additional porogen from the precursor film thereby completing formation of the porous low-k dielectric film. In many embodiments, the dielectric constant of the porous low-k dielectric film after (c) is about 2.5 or lower.

In one embodiment, the precursor film is formed by co-depositing the porogen with the structure former. The porogen is frequently an organic material and the structure former a silicon-containing material. As general examples, the structure former can be produced from silanes, alkylsilanes (*e.g.*, trimethylsilane, di-*tert*-butylsilane and tetramethylsilane), alkoxysilanes (*e.g.*, methyltriethoxysilane (MTEOS), methyltrimethoxysilane (MTMOS) diethoxymethylsilane (DEMS), methyltrimethoxysilane (MDMOS), trimethylmethoxysilane (TMMOS) and dimethyldimethoxysilane (DMDMOS)), linear siloxanes, cyclic siloxanes (*e.g.* octamethylcyclotetrasiloxane (OMCTS) and tetramethylcyclotetrasiloxane (TMCTS)), silylalkenes (*e.g.*, vinyltrimethylsilane (VTMS)), silylalkynes (*e.g.*, trimethylsilylacetylene (TMSA), bis-trimethylsilylacetylene (BTMSA), or a combination thereof. These compounds can form carbon-doped oxides (CDOs), sometimes referred to as organosilicate glasses (OSGs).

One preferred class of porogen compounds is the polyfunctional cyclic non-aromatic compounds. Examples of such compounds are pienes such as beta-piene and alpha-piene. Additional preferred porogen compounds include compounds with multiple reactive sites, such as  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}=\text{CH}-$ ,  $-\text{C}\equiv\text{CH}$ ,  $-\text{C}\equiv\text{C}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{OCH}_3$ . Typical examples of these compounds are 1,2,3,4-tetramethyl-1,3-cyclopentadiene (TMCP) ( $\text{C}_9\text{H}_{14}$ ), 5-ethylidene-2-norbornene (ENB) ( $\text{C}_9\text{H}_{12}$ ) and methyl methacrylate (MMA). Another class of porogen compounds is template forming compounds such as certain block copolymer materials used

to form ordered mesoporous films. In a somewhat different approach, the porogen and structure former exist in the same precursor molecule. After creating a precursor layer of such material, the layer is treated to remove the porogen from the composition, while leaving the structure former. Examples of these types of compounds are various organic silanes, such as di-*tert*-butyl-silane, that possess bulky organic groups. The *tert*-butyl group can be driven from the deposited silicon-oxygen matrix to leave behind small pores. Additional examples include 5-(bicycloheptenyl)methyldimethoxysilane (BMDS) ( $\text{SiC}_{10}\text{O}_2\text{H}_{18}$ ) and 5-(bicycloheptenyl)triethoxysilane (BTS) ( $\text{SiC}_{13}\text{O}_3\text{H}_{24}$ ). Generally, the precursor film in (a) can be formed using any number of different processes. Many implementations involve CVD processes (*e.g.*, a plasma enhanced chemical vapor deposition (PECVD) technique). Other deposition techniques include spin-on processes and other condensed phase techniques.

In some embodiments the plasma in (b) removes between about 5% and about 90% of the porogen from the precursor film. This greatly reduces the amount of porogen that is expelled from the film during the treatment in (c). The plasma may be formed under any suitable conditions. In some cases, the plasma comprises hydrogen, helium, argon, nitrogen, carbon dioxide gas or a combination thereof. Preferred flow rates range, for example, between about 100 and about 10,000 sccm in a six wafer Sequel<sup>®</sup> PECVD chamber. A preferred pressure range, for example, is between 0.5 Torr and 20 Torr. In some embodiments, the plasma in (b) can be provided by a dual RF source with a high frequency component power ranging between about 0.1 and about 20  $\text{W}/\text{cm}^2$  and a low frequency component power ranging between about 0.1 and about 20  $\text{W}/\text{cm}^2$  (determined per unit surface area of the substrate being treated). In other embodiments the source is a single frequency source. In preferred embodiments, the substrate temperature during plasma exposure in (b) is between about 100 and about 500 degrees Celsius. Typical plasma exposure times range between about 1 second and about 30 minutes.

In some embodiments, the first and second chambers are separate chambers in a multi-chamber apparatus. In such cases, the first and second chambers are commonly vacuum integrated. In other embodiments, the first and second chambers are provided as

separate stand-alone apparatuses. Substrate transfers from chamber to chamber may be done by utilizing a robot wafer handler, for example.

In applications where thicker films are desired, operations (a) and (b) can be repeated a number of times to build up a desired thickness of the precursor film before the treatment in (c) is performed.

Operation (c) (to further remove porogen and improve film mechanical properties) is preferably a UV radiation or e-beam treatment. If a UV radiation treatment is used, the UV radiation may comprise a spectra peak at a wavelength at or near an absorption peak of the porogen. But usually the spectral distribution is chosen to provide optimal mechanical strengthening. In typical applications, the UV radiation comprises a wavelength or distribution of wavelengths within the range of about 156 nm to about 500 nm. The UV radiation intensity for typical applications is at least about 200 mW/cm<sup>2</sup> and typical exposure times range between about 1 second and about 30 minutes. During UV radiation exposure, a preferred substrate temperature ranges between about 25 and about 450 degrees Celsius. UV exposure preferably occurs in controlled environments, such as vacuum conditions with purging gases to maintain the desired pressure. The examples of purging gases include inert gases, e.g. helium, argon, etc, or porogen reducing gases, e.g. CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, etc.

These and other features and advantages of the invention will be described in more detail below with reference to the associated drawings.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

The following detailed description can be more fully understood when considered in conjunction with the drawings in which:

Figure 1 is a flowchart summarizing processing stages in example implementations  
5 of the invention.

Figure 2 is a schematic representation of an apparatus suitable for some embodiments of this invention.

Figure 3 is a graph showing FTIR spectra of precursor films before and after plasma treatment for porogen removal.

10 Figures 4A-4C are graphs representing amounts of porogen removed from film as a function time with plasma treatment, UV treatment and thermal treatment.

Figures 5A-5B are graphs representing film thickness loss, dielectric constant and hardness as a function of UV treatment time for a film not previously treated and for a film previously treated with plasma.  
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## DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

### INTRODUCTION

In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention, which pertains to porogen removal of a porous precursor film. The porous precursor film may comprise a carbon-doped oxide (CDO) or organosilicate glass (OSG). The present invention may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail to not unnecessarily obscure the present invention. While the invention will be described in conjunction with the specific embodiments, it will be understood that it is not intended to limit the invention to the embodiments.

The present invention involves forming a low-k dielectric material by way of a “precursor film” or “precursor layer” that contains a “structure former,” typically a dielectric material, which serves as a backbone of the porous network, and a porogen, which generates the porous regions within the dielectric film. Hence, the porogen and dielectric matrix typically exist as separate phases within the precursor layer. In methods of this invention, the porogen is removed from the precursor film to create a porous low-k dielectric layer. Within the precursor film, the porogen resides in locations that will subsequently become void locations in the final dielectric film.

Methods of the invention also involve increasing the “mechanical strength” of the porous low-k dielectric layer. Mechanical strength may be manifest in terms of hardness, modulus, intrinsic stress, cohesive strength, etc. Intrinsic stress, hardness and modulus are well defined within the art and will not be discussed in detail herein. Measures of film hardness presented herein may be made with any suitable apparatus including a nano-indenter device. Measure of intrinsic film stress may be made with any suitable apparatus including a stress gauge.

One way to characterize cohesive strength in a dielectric layer is via a “cracking threshold” measurement. This is a measure of thickness of a dielectric film on a blank substrate (*e.g.*, a flat 200 or 300 mm wafer) that can be deposited without forming a crack. In a typical experiment, the dielectric is deposited to various thicknesses using a single set of process conditions. The resulting wafer (with dielectric layer) is set aside without disturbance for a period of time (*e.g.*, one day) and then examined for cracks. The greatest

thickness at which no crack is observed is the cracking threshold. For many processes, the cracking threshold is measured in micrometers.

The precursor film may be formed by any of numerous techniques. In some methods, the structure former and porogen are co-deposited in one process. Any suitable deposition technique may be used, including spin-coating processes, print-on, dip coating, thermal process and chemical vapor deposition – particularly plasma enhanced chemical vapor deposition (PECVD). In alternative methods, the structure former and porogen are deposited separately in a two-phase process. For example, in some mesoporous films, a template-forming precursor, solvent and catalyst are mixed and applied by spin-coat or print-on methods to form a template in a first process phase, then a silica-forming precursor is introduced to the formed template in a second process step such as supercritical infusion into a polymer matrix. Depending on the application, the thickness of the precursor film may range between about 30 nanometers and 3 micrometers.

Generally, a porogen is any removable material that defines void regions in a dielectric matrix. Frequently, though not necessarily, the porogen is an organic material. Methods to remove porogen from the precursor film include use of a plasma (e.g., hydrogen plasma), by a UV mediated method and thermal methods. In many embodiments of this invention, a significant amount of the porogen in a precursor layer is removed by exposure to a plasma within the same chamber in which the layer was formed.

Various UV radiation methods for removing porogen are described in related applications referred to previously and which are incorporated in their entirety within. UV radiation methods can be used in two general ways for porogen removal. In a first approach, the UV light directly interacts with the porogen to chemically decompose or otherwise modify the porogen and produce products that are more easily removed than the porogen itself. In another approach, the UV exposure occurs in the presence of oxygen to create an oxidizing environment (e.g., ozone and/or oxygen radicals) that oxidizes the porogen. The oxidation products are more easily removed than the porogen itself. Note that in this approach, some UV radiation may interact directly with the porogen as well. In general, the UV radiation is tuned for absorption by the porogen in the first approach and tuned for oxygen activation in the second approach. Thus, in the first approach, the UV radiation preferably has a high intensity component at a wavelength (or range of wavelengths) at or near an absorption peak of the porogen. Of course, the porogen may be chosen to match the characteristics of an available UV source. In many embodiments of this invention, UV

mediated porogen removal occurs during a mechanical strengthening process – after some fraction of the porogen was initially removed using plasma.

Any suitable plasma that can directly or indirectly cause the breakdown of chemical bonds in the porogen may be used. Reducing or oxidizing gases may be used, although reducing gases are preferred. Suitable gases include hydrogen, NH<sub>3</sub>, CO<sub>2</sub> and O<sub>2</sub>.

In some cases the porogen is randomly distributed throughout the precursor film and other cases it is ordered in a repeating structure throughout the film. In the case of an ordered porous or mesoporous dielectric matrix, the porogen is frequently referred to as a “template.” One type of ordered porogen, for example, is a block copolymer that has chemically distinct components (*e.g.* PEO polyethylene oxide and PPO polypropylene oxide) that segregate into separate phases. The discussion herein will refer to porogen and porogen materials in general and are intended to include any type of porogen, ordered or non-ordered, organic or inorganic, unless otherwise specified.

Frequently, the porogen is a hydrocarbon. The following is a non-comprehensive list of precursor films (listed by type of porogen molecules) suitable for the present invention. “Low temperature porogens” are deposited below about 200 degrees C and “high temperature porogens” are deposited above about 200 degree C.

Low Temperature Porogens	High Temperature Porogens
Aldehydes: CH <sub>2</sub> O, CH <sub>3</sub> CHO	Alkenes: C <sub>2</sub> H <sub>4</sub> , CH <sub>3</sub> -CH=CH <sub>2</sub> , etc
Alkenes: C <sub>2</sub> H <sub>4</sub> , CH <sub>3</sub> -CH=CH <sub>2</sub> , etc	Terpinene compounds ( <i>e.g.</i> , alpha-terpinene)
di-tert-butyl silane	Pinene compounds ( <i>e.g.</i> , alpha and beta)
Esters	Compounds with multiple active sites ( <i>e.g.</i> , ENB)

One preferred class of porogens is the polyfunctional cyclic non-aromatic compounds, particularly 5-ethylidene-2-norbornene (ENB) and pinene compounds, including alpha and beta pinene isomers. Other polyfunctional cyclic non-aromatic compounds include alpha terpinene compounds include, for example, alpha-terpinene compounds and derivatives thereof. Other compounds include functional groups such as -CH=CH<sub>2</sub>, -CH=CH-, -C≡CH, -C≡C-, -C=O, -OCH<sub>3</sub>. Typical examples of these compounds are 1,2,3,4-tetramethyl-1,3-cyclopentadiene (TMCP) (C<sub>9</sub>H<sub>14</sub>) and methyl methacrylate (MMA). Three-dimensional functional compounds such as 5-ethylidene-2-norbornene (ENB) are preferred. These compounds have at least three active sites to allow formation of a three-dimensional network.

In some cases, the porogen and structure former reside in the same compound. That is, the porogen is a removable moiety in a compound that contains moieties serving as structure formers covalently bonded to moieties serving as the porogen. Nominally, the porogen moiety is a large bulky organic group that will leave pores in the resulting dielectric film. Examples of such species are organic silanes such as di-*tert*-butylsilane, phenyldimethylsilane, and alkoxysilanes such as 5-(bicycloheptenyl)methyldimethoxysilane (BMDS) and 5-(bicycloheptenyl)triethoxysilane (BTS) ( $\text{SiC}_{13}\text{O}_3\text{H}_{24}$ ). These compounds may be deposited using CVD or spin on methods, for example. As indicated, the structure former serves as a backbone for the resulting porous low-k film.

Many different chemical compositions may be used as the structure former. In some embodiments, the composition includes silicon and oxygen. Sometimes it also includes carbon (as in CDOs or OSGs) and/or other elements (e.g., fluorine) and even metals (e.g., germanium). For relatively thick precursor layers, it will sometimes be desirable to use structure formers that are not opaque to the UV radiation.

Examples of precursors for structure formers include silanes, alkylsilanes (e.g., trimethylsilane, di-*tert*-butylsilane and tetramethylsilane), alkoxysilanes (e.g., methyltriethoxysilane (MTEOS), methyltrimethoxysilane (MTMOS) diethoxymethylsilane (DEMS), methyldimethoxysilane (MDMOS), trimethylmethoxysilane (TMMOS) and dimethyldimethoxysilane (DMDMOS)), linear siloxanes and cyclic siloxanes (e.g. octamethylcyclotetrasiloxane (OMCTS) and tetramethylcyclotetrasiloxane (TMCTS)).

The thickness of the precursor film (and hence the resulting dielectric layer) depends upon the ultimate application – and recognizing that the film typically shrinks to some degree during porogen removal and/or strengthening treatments. As an example, the thickness may range between about 50 to 1500 angstroms for a hard mask application. For an interlayer dielectric or packaging application, the thickness may range from 1500 angstroms up to about 2 to 3 microns (typically 2000 to 5000 Angstroms). In some cases, extra thickness is required to provide some amount of sacrificial dielectric to accommodate a subsequent planarization or polishing step. In some cases, the thickness of the precursor layer may be driven in part by the ability of the plasma and/or UV radiation to penetrate the film and remove the porogen. In these cases, the sequence of precursor film deposition followed by plasma exposure may be repeated several times to achieve the desired final thickness.

It will be appreciated by those skilled in the art that the UV radiation used with the invention encompasses near-UV, as well as UV wavelengths. Methods of the invention utilize UV radiation for various operations including facilitating porogen removal, reconstructing chemical bonds to mechanically strengthen the dielectric film, and facilitating cleaning of the reaction chamber. Some operations may more effectively be implemented using UV light with a particular range of wavelengths, *i.e.*, wavelength distribution. For instance, a wavelength distribution appropriate for interacting with a porogen for porogen removal from a precursor film may differ from the wavelength distribution appropriate for interacting with oxygen gas molecules to create ozone and oxygen radicals to clean the walls of a reaction chamber. In addition, some operations may more effectively be implemented using UV light having at least a predefined intensity, sometimes referred to as a threshold intensity. The threshold intensity for any particular film can vary depending upon numerous factors such as UV exposure time, film type and process conditions. For purposes of the invention, light intensity is measured in terms of power density (in mW/cm<sup>2</sup>). Details as to how power density is measured will be described later. For chamber cleaning, any precursor that can be dissociated by UV light and can attack any residual deposition from UV process may be used.

## PROCESS

Figure 1 is a flow chart depicting one general high-level process flow in accordance with some embodiments of the present invention. Initially, a precursor film is provided on a substrate as indicated by a process block 101. As mentioned previously, a precursor film contains a porogen and a structure former for the dielectric backbone. In many embodiments of commercial application, the substrate is a partially fabricated integrated circuit or other partially electronic semiconductor device.

As described above, various techniques for forming a precursor film may be employed. A typical approach involves co-depositing the porogen with the structure former precursor using a low temperature PECVD (plasma enhanced chemical vapor deposition) process. As indicated, other processes such as high temperature chemical vapor deposition methods and spin-on methods may be employed. Other suitable deposition techniques include supercritical infusion, print-on, and dip coating. It is noted again that the invention is not limited to any particular type of deposition method. However, when the initial porogen

removal involves a plasma treatment in the chamber where the deposition took place, a PECVD process is generally preferred.

Returning to Figure 1, the precursor film is exposed to a plasma to remove a substantial portion of the porogen. See process block 103. Preferably this is performed while in the same chamber that the precursor film was formed. The reaction chamber may be any suitable chamber capable of forming and confining a plasma. As suggested above, the chamber may be a PECVD chamber. In typical embodiments, between about 5% and 90%, preferably between about 50% and 90% of the porogen is removed during operation 103. A goal is to remove sufficient quantities of porogen during operation 103 that a subsequent treatment to improve mechanical strength does not expel significant quantities of porogen.

As mentioned previously, the plasma can be generated from any suitable gas that can create chemical species capable of reacting with the porogen or otherwise facilitating its removal. Typically, the chemical species in the plasma decompose the porogen into lower molecular weight components that can be vaporized and thereby be removed from the precursor film. The gases may be oxidizing gases, such as oxygen, nitrous oxide, and carbon dioxide. Alternatively, reducing gases may be used, such as hydrogen and  $\text{NH}_3$ . The gases may be also inert gases, such as  $\text{N}_2$ , He and Ar.

The plasma may be characterized by various parameters including plasma intensity, temperature, pressure, flow rates of the gases that produce the plasma, exposure time, etc. Flow rates of gases can vary broadly depending upon numerous factors including apparatus configuration. In a specific example using a Sequel C-2<sup>®</sup> chamber (available from Novellus Systems of San Jose, CA), preferred flow rates of hydrogen gas ranged between about 100 and about 10,000 sccm. Typically a dual frequency RF plasma source is used to produce the plasma. In a specific example, a high frequency component (e.g., at or about 13 MHz) is provided at a power between about 0 and about 5000 Watts and a low frequency component (e.g., at or about 275 kHz) is provided at a power between about 0 and about 1500 Watts. Substrate temperatures may also vary depending upon the type of application and other factors. Typical acceptable substrate temperatures for integrated circuit applications range between about 200 and about 500 degrees Celsius. In some embodiments, the substrate is electrically biased. Substrate exposure time to the plasma may vary depending upon any of a number of factors such as gas type and flow rate, precursor type and thickness, plasma powers and substrate bias. In a typical integrated circuit application, plasma exposure may range between about 5 seconds and 30 minutes.

Referring back to Figure 1, after the substrate is exposed to the plasma to remove at least a significant portion of porogen from the precursor film, the next operation is a treatment to improve the mechanical strength of the porous dielectric film in a second chamber. In preferred embodiments, this is accomplished by exposing the film to UV radiation. See block 105. Note, however, that the invention is not limited to UV radiation procedures and other suitable procedures, such as electron beam (e-beam) methods, may be used. If e-beam methods are used, the apparatus should have appropriate components such as e-beam generator as well as elements for focusing and/or directing the e-beam. In other embodiments, combinations of techniques are used to mechanically strengthen the film.

The second chamber may be a chamber in a separate stand-alone apparatus or it may be a different chamber in a multi-chambered apparatus. In some embodiments, the first and second chambers are vacuum integrated to prevent wafer exposure to ambient and contaminants between operations and/or to improve wafer throughput. In a typical apparatus set-up, a robot is used to transfer the substrate wafer between the first and second chambers. An example of a suitable apparatus will be described further.

As mentioned previously, the present invention provides a means to ensure that UV chambers and related chambers used for treating porous low-k materials to increase the mechanical strength of the materials remain clean during the manufacturing process. Since a substantial portion of porogen can be removed in the first chamber (typically a PECVD chamber), this will minimize porogen-related residues and buildup inside chamber walls and other components within the chamber used for mechanically strengthening the film. The bulk of the residue buildup can then be more easily managed by periodic clean up of the first chamber, typically a PECVD chamber that can be cleaned with a plasma treatment with fluorine containing chemicals. In embodiments where a UV radiation apparatus is used to mechanically strengthen the film, one component in particular that should be kept clean from residues is the inside surface of windows (typically quartz) used for allowing in UV radiation. As additional residues build up on the window, less UV energy can reach the wafer to be treated. Similarly, in an e-beam apparatus, the build up of porogen residues on the e-beam gun or source will reduce the e-beam generating efficiency. As an example, in methods that do not remove porogen prior to UV or e-beam treatment, the second chamber must be cleaned after treating every 2-10 wafers. By removing porogen prior to the UV or e-beam chamber, the cleaning is required much less frequently, e.g., after about 100-200 wafers are treated.

Another advantage of using the methods of the invention is that wafer throughput can be improved. Since the precursor film formation and plasma porogen removal occur in the same chamber, less time is needed for pumping down systems and transferring wafers. In addition, it has been found that removing a substantial portion of porogen using plasma methods can shorten the UV radiation exposure time, thereby increasing the overall wafer throughput. Removal of porogen using plasma methods is also found to be faster than thermal annealing methods. Experimental data showing this aspect will be described later (see Figures 4A, 4B and 4C and related discussion). Further, it is desirable to reduce the UV exposure time during operation 105. It has been found that extended UV exposure times can lead to film shrinkage and/or thickness loss, which can eventually cause the film to crack. Experimental data showing this aspect will be discussed further (see Figures 5A and 5B and related discussion).

In embodiments in which UV radiation is used to increase the mechanical strength of the film, the UV radiation preferably uniformly irradiates the wafer substrate so as to provide even exposure of the precursor film. The UV radiation may comprise any wavelength distribution appropriate for mechanically strengthening the dielectric portion of the film. In addition, the UV radiation preferably comprises a spectral peak at a wavelength at or near an absorption peak of the porogen so that at least a portion of any remaining porogen in the film may be volatilized. Appropriate wavelength distributions typically range between about 156 nm to about 500 nm.

Suitable UV sources (as characterized by wavelength distributions and light intensities) can be chosen based upon a number of factors including the dielectric film thickness and composition as well as the desired hardness and dielectric constant of the resultant film.

For a typical OSG film of with a thickness ranging between about 1500 and 10000 Angstroms, for example, preferable exposure times may range between about 5 second and 30 minutes, for example. Exposure times can range from seconds to tens of hours. Preferably, for commercial applications, the exposure time will be about 5 minutes or less.

To some extent the exposure time is a strong function of the UV intensity. But below a certain threshold intensity, it has been found that little if any hardening will occur even after prolonged exposure. Numerous other factors can influence the preferred amount of UV radiation intensities including film thickness and composition. In a number of applications UV radiation intensities are preferably at least 100 mW/cm<sup>2</sup>. The wafer substrate

temperature may influence the hardening process. In some embodiments, higher temperatures may be more effective, but the temperature should not be too high as to cause damage to the substrate device. In general, temperatures below about 450 degrees C are preferable, more preferably  $\leq 400$  degrees C, as higher temperatures can damage a partially  
5 fabricated device, particularly one that employs copper lines. Typical temperatures range between about room temperature (*i.e.*, 20 degrees C) up to 450 degrees C. It should be noted that exposure to UV radiation can itself contribute to substrate heating. UV exposure preferably takes place in an inert environment, for example, under vacuum conditions.

UV treatments in accordance with this invention may sometimes improve other  
10 mechanical properties besides just hardness. For example, they may reduce internal stress in the dielectric film. Preferably, the internal stress, as measured by cracking threshold, is at least about 4 micrometers.

In some embodiments, operations 101 (providing a precursor film) and 103 (exposure to plasma to remove a portion of porogen) are repeated a number of times to build  
15 up the desired thickness of film for the particular application before transferring the substrate to a second chamber for implementing operation 105.

After operation 105, the process flow of Figure 1 is complete. Note that at this point, the reaction chamber may also optionally be cleaned of porogen residues. A suitable UV chamber cleaning procedure is described further in US Patent Application No.  
20 \_\_\_\_\_ (Attorney Docket No. NOVLP089), which this application claims priority from and which is incorporated in its entirety herein. For example, one suitable cleaning treatment described involves UV radiation in combination with an oxidative gas.

A suitable apparatus in accordance with the present invention will now be described.

## 25 APPARATUS

The present invention can be implemented in many different types of apparatus. In preferred embodiments, the apparatus will include one or more chambers (sometimes referred to as process vessels) that house one or more wafers and are suitable for wafer processing. At least one chamber will include a plasma source. A single chamber may be  
30 employed for all operations of the invention or separate chambers may be used. Each chamber may house one or more wafers for processing. The one or more chambers maintain

the wafer in a defined position or positions (with or without motion within that position, *e.g.*, rotation, vibration, or other agitation) during procedures of the invention. For certain operations in which the wafer is to be heated, the apparatus may include a heating platen.

Figure 2 is a schematic diagram of one specific example multi-chambered apparatus that may be employed to implement the invention. Apparatus enclosure 201 comprises two separate types of chambers, a PECVD chamber 203 and a UV radiation chamber 205. A robot wafer handler 237 is positioned for transferring wafers (*e.g.*, wafer 235) between chamber 203 and chamber 205. Apparatus enclosure 201, which encloses chambers 203 and 205 and robot wafer handler 237, can be entirely evacuated using vacuum pump system 206. This configuration is consistent with many cluster-type tools in the industry.

As shown in Figure 2, the apparatus is capable of simultaneously processing multiple wafers in PECVD chamber 203. PECVD chamber 203 is capable of holding a vacuum and can be separately evacuated with vacuum pump system 225. As indicated by slash-through 202, PECVD chamber 203 may comprise more than two stations for processing wafers. For simplicity, only two stations are shown. For example, one station comprises wafer station 207A with pedestal 209A that is capable of holding wafer 211A for exposure to plasma provided by showerhead 213A. Similarly, in wafer station 207B has pedestal 209B that is capable of holding wafer 211B for exposure to plasma provided by showerhead 213B. Wafer station 207A and 207B may have heating elements (not shown) that can heat the wafer to defined temperatures and be controlled by a temperature controller (not shown). Showerheads 213A and 213B each deliver mixed process gases to their associated stations and also serve as capacitive plates for generating plasmas. A generic gas source 215 supplies three types of gases to the different stations of PECVD chamber 203 via manifolds 217A and 217B.

The power delivered for generating plasmas is provided via matching networks 223A and 223B, respectively. Matching network 223A matches high and low frequencies provided by a low frequency source 219A and a high frequency source 221A to produce optimal plasma generating and maintaining frequencies for showerhead 213A. Similarly, matching network 223B is supplied with a low frequency source 219B and a high frequency source 221B to produce optimal plasma generating and maintaining frequencies for showerhead 213B. In some embodiments, a single high frequency source, a single low frequency source and a single matching network supply power to all stations of chamber 203.

UV radiation chamber 205 comprises a wafer holder 227, which secures wafer 229 in a position such that light from a UV light source 231 can irradiate wafer 229. Chamber 205 may be separately evacuated using vacuum system 226. Window 233 allows UV radiation from UV light source 231 to enter chamber 205. Note that window 233 may be composed of any suitable material for letting UV light pass, including quartz and sapphire. Filters can also be used to remove unwanted spectral components from particular sources to “tune” the sources for particular applications (e.g., porogen removal, dielectric hardening, or chamber cleaning). Wafer holder 227 can have a heating element (not shown) that can heat the wafer to defined temperatures and can be controlled by a temperature controller (not shown). UV radiation chamber 205 is configured with a gas inlet (not shown), which is connected to a gas source (not shown). The amount of gas introduced into UV radiation chamber 205 can be controlled by a valve (not shown) and is measured by pressure gauge (not shown). Note that gas source 208 may also provide gas to UV radiation chamber 205 in embodiments where it is desirable to expose the wafer to gases during UV radiation exposure. In addition, gas source 208 may provide cleaning gases, such as oxidizing gases, that can be used to clean the inside of UV radiation chamber and window 233 after the wafer 229 is removed.

Note that UV light source 231 may be a single UV source or an array of UV sources, such as an array of UV lamps. In this example, UV light source 213 is mounted outside the chamber 205. In alternate embodiments, the UV light source array is housed inside chamber 205. Note that the invention is not limited to any particular types UV light sources. Suitable UV sources include xenon, mercury and deuterium lamps or lasers (e.g., excimer lasers and tunable variations of various lasers). Various optical elements may be required to direct the UV light toward portions of the substrate. Methods for directing the light at different portions of the substrate at different times will be required as well. A scanning mechanism may be used for this purpose. Examples of other suitable UV chamber apparatus configurations are presented in US Patent Application No. \_\_\_\_\_ (Attorney Docket No. NOVLP089), which this application claims priority from and which is incorporated in its entirety herein.

A typical process during normal operation of the apparatus in accordance with the invention will now be described. Note that the description is only one example of a typical operation and other operations with more, less, or different procedures may be implemented. First, wafers are transferred into apparatus enclosure 201 and it is evacuated using vacuum system 206. Next, the wafers are transferred into PECVD chamber 203 at a particular station and the chamber is closed. Then appropriate porogen precursor and structure former

precursor gases are introduced to different stations within PECVD chamber 203 from gas source 215 via manifolds 217A and 217B. Power at the desired frequencies is supplied by matching networks 223A and 223B and is applied to the capacitive plates in showerheads 123A and 123B, respectively. Plasmas are then generated near wafers 211A and 211B and the porogen precursor and structure former precursor are co-deposited to form precursor films on wafers 211A and 211B. After the precursor films are deposited, the flow of gases is stopped, the plasma sources are turned off, and PECVD chamber 203 is evacuated using vacuum system 225.

Next, hydrogen gas from gas source 215 is introduced into PECVD chamber 203 via manifolds 217A and 217B. Power at the correct frequencies is supplied by matching networks 223A and 223B and is applied to the capacitive plates in showerheads 123A and 123B, respectively. Hydrogen plasmas are then generated near wafers 211A and 211B and substantial portions of the porogen from precursor films on wafers 211A and 211B are volatilized. After a sufficient length of time, the process is concluded and PECVD chamber 203 is then evacuated using vacuum pump system 225.

PECVD chamber 203 is then opened and one of wafers 211A and 211B, e.g., wafer 211A, is removed from PECVD chamber 203 using robot wafer handler 237 and placed onto wafer holder 229 in UV radiation chamber 205. UV radiation chamber 205 is then closed and evacuated, if necessary, using vacuum pump system 226. Alternatively, an inert gas (e.g., argon, nitrogen) is introduced from gas source 208 to a certain chamber pressure. UV source 231 is then powered on and UV light shines through window 233 to expose wafer 211A on pedestal 227 to mechanically strengthen and remove portions of any remaining porogen in the precursor film of wafer 211A. After the film is sufficiently treated, UV source 231 is powered off and UV radiation chamber 205 is further evacuated using vacuum pump system 226 to remove volatilized porogen residues.

UV radiation chamber 205 is then isolated from vacuum by a valve in vacuum pump system 226 and opened to the vacuum conditions provided in apparatus enclosure 201. Wafer 211A is then removed from UV radiation chamber 205 using robot wafer handler 237 and wafer 211B is then placed in UV radiation chamber 205 for similar processing. Subsequent wafers are processed similarly in this sequence.

In some cases, it will be desirable to apply the precursor layer and remove porogen in multiple iterations – all prior to the UV treatment. In this manner, the porogen can be removed more completely, albeit gradually. By using a multi-station tool such as chamber

203, the process may treat the wafer in multiple iterations as described. At each station, a wafer receives a sub-layer of the precursor material (network former and porogen) and then is plasma treated to remove at least a portion of the porogen in that sub-layer. The wafer may then be indexed to the next station where an additional sub-layer is deposited and treated with plasma. Eventually, the full thickness of precursor layer is deposited and plasma treated. At this point, the wafer is removed from chamber 203 and transferred to chamber 205.

## EXPERIMENTAL DATA

Figure 3 shows a composite graph of two FTIR spectra, one of a precursor film before treatment (top spectrum) and one of precursor film after a hydrogen plasma treatment (bottom spectrum). In this case, the treated film was exposed to hydrogen plasma for about 2 minutes with at pressures about 3 Torr, high frequency power of about 1800 W, H<sub>2</sub> flow rate of about 1000 sccm and N<sub>2</sub> flow rate of about 3000 sccm using a Sequel<sup>®</sup> C-2 PECVD tool. The precursor film was formed by co-depositing diethoxymethylsilane (DEMS) and 5-ethylidene-2-norbornene (ENB) using carbon dioxide as a carrier gas.

The FTIR spectrum of the untreated film (top) exhibits an absorption peak corresponding to C-H stretch around 2780 cm<sup>-1</sup> to 3050 cm<sup>-1</sup> attributed to the hydrocarbon porogen within the precursor film. The plasma treated film (bottom) shows that the C-H stretch peak is reduced. Also shown in both spectra are Si-CH<sub>3</sub> methyl rocking bands at around 1271 cm<sup>-1</sup> attributed to (SiO)<sub>3</sub>Si-CH<sub>3</sub> groups. As shown, the amplitude of this peak was also reduced in the film after hydrogen plasma treatment (bottom) compared to before treatment (top), indicating the plasma treatment resulted in more crosslinking and mechanical strengthening of the carbon-containing dielectric matrix. It should be noted, however, that although some mechanical strengthening has occurred using hydrogen plasma treatment, it is desirable to further strengthen the matrix to provide an adequately robust porous film for many integrated circuit applications.

Also within spectra of Figure 3 are peaks at 1039 cm<sup>-1</sup> attributed to smaller angle (<144°) Si-O-Si stretching in the OSG matrix, at 1065 cm<sup>-1</sup> attributed to ~ 144° angle of Si-O-Si network and at 1135 cm<sup>-1</sup> attributed to larger angle Si-O-Si stretching in the cage structures of the network (bond angles of approximately 150°). Peak at 1065 cm<sup>-1</sup> and peak at 1135 cm<sup>-1</sup> are overlap each other. The cage structure peak (1135 cm<sup>-1</sup>) was reduced after

hydrogen plasma treatment, which could be due to the formation of new chemical bonds within the OSG matrix.

Figures 4A-4C are graphs comparing the effective removal of porogen from precursor films using hydrogen plasma (Figure 4A), UV radiation (Figure 4B) and thermal anneal treatments (Figure 4C). Each of the precursor films was formed by co-depositing diethoxymethylsilane (DEMS) and 5-ethylidene-2-norbornene (ENB) using carbon dioxide as a carrier gas. Data from Figures 4A-4C are for one wafer processed at a time. Each graph shows the ratio of the areas of  $\text{CH}_X$  to  $\text{SiO}$  peaks,  $[\text{CH}_X]/[\text{SiO}]$ , in the FTIR spectra (y-axes) as a function of treatment time in minutes (x-axes). The  $\text{CH}_X$  peaks include  $-\text{CH}_3$  and  $-\text{CH}_2$  from the carbon-containing dielectric network and  $-\text{CH}_3$ ,  $-\text{CH}_2$  and  $-\text{CH}$  groups from the porogen. As such,  $[\text{CH}_X]/[\text{SiO}]$  derived from the FTIR spectra provide a general indication of the amount of porogen in the film.

Figure 4A shows  $[\text{CH}_X]/[\text{SiO}]$  of a precursor film as a function of hydrogen plasma exposure time. Reaction chamber pressures were about 3 Torr, high frequency power was about 1800 Watts, hydrogen gas dosage was about 1000 sccm, nitrogen gas dosage was about 3000 sccm and substrate temperature was about 400 degrees Celsius. As shown,  $[\text{CH}_X]/[\text{SiO}]$  decreases with increasing hydrogen plasma treatment time, with about 50% of the porogen removed by 1 minute, with a significant amount removed within 10 seconds. The concentration of  $\text{CH}_X$  decreases very slowly after 1 minute. Note that this data was provided in a 6-station PECVD apparatus. So the equivalent exposure time can be divided by six. For example, in the 6-station PECVD apparatus, the amount of porogen removed from six wafers after 60 seconds of hydrogen plasma exposure would roughly correspond to the amount of porogen removed from one wafer after 10 seconds exposure. In other words, about 50% of the porogen were removed after about 10 seconds/per station.

Figure 4B shows  $[\text{CH}_X]/[\text{SiO}]$  of a precursor film as a function of UV exposure time. A xenon lamp was used as the UV source and the UV intensity incident upon the wafer was about  $1.75 \text{ W/cm}^2$ . As shown by the graph of Figure 4B, porogen removal efficiency was similar to that using hydrogen plasma (Figure 4A). That is, much of the porogen was quickly removed (about 10 seconds per station). Relatively little porogen was removed after that point.

Figure 4C shows  $[\text{CH}_X]/[\text{SiO}]$  of a precursor film as a function of thermal annealing time. Thermal annealing was done by heating the wafer to about 425 degrees Celsius under vacuum conditions. As shown, thermal annealing takes considerably more time to remove

porogen than either hydrogen plasma treatment or UV radiation exposure. For example, more than 50 minutes of annealing time was needed to remove most of the porogen with significant amounts of porogen still being removed after 50 minutes of annealing time.

Figures 5A and 5B present data showing the effects of UV treatment on film thickness loss, dielectric constant (k) and hardness. All films were deposited from DEMS and ENB a with high power frequency of about 2200 W, CO<sub>2</sub> flow rate of about 3000 sccm, pressure 7.5 Torr, DEMS flow rate of about 0.9 sccm and ENB flow rate if about 0.9 ccm.

Figure 5A shows the % film thickness loss for two films exposed to UV radiation, one that had previously been treated with hydrogen plasma (diamond symbols) and one that had not been previously treated (square symbols). As shown, the film previously treated with hydrogen plasma experienced less thickness loss than the film not previously treated.

Figure 5B shows data illustrating the effects of UV exposure time on the dielectric constant (k) and hardness (H). Hardness was measured in GigaPascals (GPa) by way of a nano-indenter device. As with the samples of Figure 5A, two films were used, one previously treated with hydrogen plasma (k represented with triangle symbols, H represented with asterisk symbols) and one not previously treated (k represented with diamond symbols, H represented with square symbols). As shown, k and H increased with increasing UV treatment time for both films. Note that only one data point for k and H were measured for the film previously treated with hydrogen plasma. However, the data suggests that the film previously treated with hydrogen plasma require less subsequent UV exposure time to achieve the same k and H values as the film not previously treated.

For example, the film previously treated with hydrogen plasma had a k value of about 2.53 and H value of about 1.34 GPa after 2.5 minutes of UV exposure. Whereas, the film not previously treated required 5 minutes of UV exposure to achieve a k value of about 2.5 and H value of about 1.32 GPa. That is, the film previously treated with hydrogen required half the UV exposure time.

While this invention has been described in terms of several embodiments, there are alterations, modifications, permutations, and substitute equivalents, which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, modifications, permutations, and substitute equivalents as fall within the true spirit and

scope of the present invention. The use of the singular in the claims does not mean “only one,” but rather “one or more,” unless otherwise stated in the claims.